

Formation of gas hydrates from single-phase aqueous solutions

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Abstract

Experiments and theory both demonstrate that crystalline hydrates can form from a single-phase system consisting of liquid water with dissolved hydrate former under appropriate conditions of temperature, pressure, and dissolved hydrate former content. At these conditions, the pressure required for hydrate formation will be equal to or greater than that required when a separate gas or liquid phase of hydrate former is present. It is possible to form hydrates from a single phase when the mole fraction of dissolved hydrate former is greater than the mole fraction which would exist in the water-rich liquid phase at the three-phase (vapor/water-rich liquid/hydrate or VLH) hydrate equilibrium pressure. However, this would represent non-equilibrium or super-saturated conditions with respect to hydrate formation. It is also possible to form hydrates from a single water-rich phase when the mole fraction of the dissolved hydrate former is less than that which would exist in the presence of a gas phase at the three-phase VLH hydrate equilibrium pressure. The pressure requirement for the formation of hydrate increases as the mole fraction of hydrate former decreases under these conditions. The possibility of forming hydrates from dissolved hydrate formers may have application to potential commercial processes; for example, in the sequestration of CO₂ in the deep ocean and in the recovery of hydrates from suboceanic and permafrost regions.

1. Introduction

Gas hydrates are crystalline solids formed from mixtures of water and low molecular weight compounds, referred to as hydrate formers, that typically are gases at ambient conditions (Sloan, 1998). Generally, hydrates are formed in the laboratory from two-phase systems by contacting a hydrate former or formers in the gas or liquid phase with liquid water and increasing the pressure until crystalline hydrate forms. However, the formation of hydrate from a single-phase aqueous system using only the hydrate former dissolved in the aqueous phase has been previously demonstrated at the National Energy Technology Center (NETL) (Warzinski, Cugini, & Holder, 1995) and more recently by Buffett and Zatsepina (2000). In addition, previous work demonstrating the equilibrium between a gaseous phase and hydrates indicates that hydrates could form from a single gaseous phase

containing sufficient gaseous water (Song & Kobayashi, 1982; Sloan, Houry, & Kobayashi, 1976).

Prior work at NETL on the impact of CO₂ hydrate on oceanic sequestration of CO₂ has shown that the initial effective density of the hydrate cluster depends on the number of phases present when the hydrates form (Warzinski et al., 1995). If CO₂ hydrate was formed from a two-phase system of either gaseous or liquid CO₂ and water, the hydrate clusters that formed were initially less dense than the aqueous phase because of the presence of free CO₂ that adheres to or is occluded in the hydrate clusters without actually being incorporated in the lattice of the hydrate. However, if the CO₂ hydrate was formed from a single-phase system consisting of CO₂ dissolved in water or seawater, the hydrate that formed was initially more dense than the aqueous phase. This would have implications in some processes being considered for injecting CO₂ into the deep ocean (> 500 m) for the purposes of non-atmospheric sequestration. Forming a sinking hydrate particle could facilitate such a process by transporting the CO₂ to depths greater than that used for injection. On the other

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hand, a rising hydrate particle would have the opposite impact.

The work reported here describes a new theoretical analysis performed at NETL relative to the formation of hydrates from single-phase aqueous systems containing dissolved hydrate former. A general thermodynamic model is presented and experimental results that describe the formation of hydrates from CO₂ dissolved in water are discussed.

2. Models for hydrate equilibrium

For calculation of hydrate formation from a single-phase water-rich liquid, the conditions where the hydrate phase is in equilibrium with the water-rich liquid are needed. At these conditions, the fugacities and chemical potentials of the species in the various phases must be equal although either equality of fugacity or chemical potential for each species is sufficient to fix the state. We specify the equality for the hydrate forming species, i , using fugacities:

$$f_{i,L} = f_{i,H} = f_i \quad (1)$$

and for water using chemical potentials:

$$\mu_H = \mu_L. \quad (2)$$

If these two conditions are met, hydrate formation can occur from a single water-rich liquid phase (no gas or liquid rich in hydrate former). Eq. (2) is modified by convention (Holder, Zetts, & Pradhan, 1988)

$$\mu^\beta - \mu_H = \mu^\beta - \mu_L \quad (3)$$

or

$$\Delta\mu_H = \Delta\mu_L. \quad (4)$$

Here, μ^β is the hypothetical chemical potential of the empty hydrate lattice.

For the hydrate-forming species, the fugacity of a dissolved gas is calculated using the traditional thermodynamic methods discussed below.

The independent (given) variables are temperature and water-rich liquid composition, i.e., the water phase contains a given mole fraction, X_i , of dissolved hydrate former. It is assumed that the solubility of the hydrate-forming species in water is known as a function of pressure from experimental data or from a model. The pressure required to obtain a given solubility, X_i , is designated P^{sat} . At pressures lower than P^{sat} the hydrate former will come out of solution as a gas bubble or possibly as a liquid drop. Due to this behavior, P^{sat} is commonly known as bubble-point pressure.

At P^{sat} , the fugacity of the hydrate former can easily be calculated from a convenient equation of state that is

applicable to a phase rich in the hydrate-forming species. For present purposes, this phase is assumed to be a gas and the Peng–Robinson equation of state is used (Peng & Robinson, 1976). Modifications needed to apply this to a liquid hydrate former are straightforward and would be necessary if the specified mole fraction can only be obtained at pressures above which the hydrate forming species is a liquid. This is not discussed further in the present analysis. At higher pressures the fugacity is corrected by a Poynting-type correction (Prausnitz, Lichtenthaler, & Gomes de Azevedo, 1986).

$$f_i = f_i^{\text{sat}} \exp \left[\int_{P^{\text{sat}}}^P \frac{\bar{V}_i dP}{RT} \right], \quad (5)$$

where \bar{V}_i is the partial molar volume of a species i in the water phase. A common assumption is that \bar{V}_i is nearly constant, thus simplifying Eq. (5):

$$f_i = f_i^{\text{sat}} \exp \left[\frac{\bar{V}_i(P - P^{\text{sat}})}{RT} \right]. \quad (6)$$

To satisfy Eq. (1), the fugacity of hydrate forming species i in the hydrate phase is set equal to f_i .

For the water species in the hydrate phase, the value of $\Delta\mu_H$ (the chemical potential of water in the hydrate phase) is calculated from the following equation (Holder et al., 1988):

$$\Delta\mu_H = -RT \sum_{j, \text{cavities}} v_j \ln \left(1 - \sum_i \theta_{ji} \right), \quad (7)$$

where v_j is the ratio of j -type cavities present to the number of water molecules present in the hydrate phase and

$$\theta_{ji} = \frac{C_{ji} f_i}{1 + \sum_i C_{ji} f_i}, \quad (8)$$

where C_{ji} is the Langmuir constant for species i in cavity j and θ_{ji} is the fraction of j -type cavities which are occupied by i -type gas molecules. The summation over species i is necessary if multiple hydrate-forming species (i.e. CH₄ and CO₂) are present.

The value of $\Delta\mu_L$ (the chemical potential difference of water in the water-rich phase) is obtained from the following equation (Holder, Corbin, & Papadopoulos, 1980):

$$\frac{\Delta\mu_L}{RT} = \frac{\Delta\mu^0}{RT_0} - \int_{T_0}^T \frac{\Delta h}{RT^2} dT + \int_0^P \frac{\Delta v}{RT} dP - \ln X_w, \quad (9)$$

where $\Delta\mu^0$ is a reference chemical potential treated as a constant whose value can change according to the gas species present. Here, Δh and Δv are the enthalpy and the volumetric difference between empty hydrate and pure liquid water, respectively. The last term accounts for the effect of dissolved gas using the mole fraction of water in the liquid phase X_w . In our analysis, the activity coefficient of water is unity.

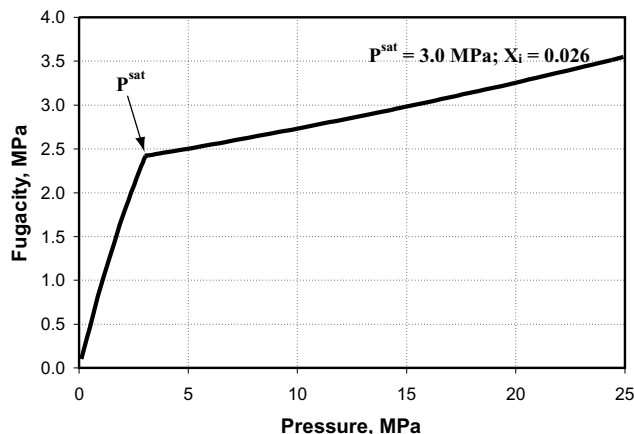


Fig. 1. The fugacity of CO₂ as a function of pressure and state. Below P^{sat} , water is presumed to have no effect on f_{CO_2} . $T = 275$ K. $\bar{V}_i = 40$ cm³/mol (estimated). X_i is the liquid-phase mole fraction of CO₂ for $P > P^{\text{sat}}$.

If $\Delta\mu_H$ from Eq. (7) equals $\Delta\mu_L$ from Eq. (9), Eq. (2) is satisfied and hydrates can form from a single-phase water-rich liquid system.

Physically, this discussion is unnecessary if hydrates will form from a gas phase at pressures less than P^{sat} . If this were possible, hydrates would form at some pressure $P < P^{\text{sat}}$ where a gas would still be present and VLH equilibria would pertain. In the experimental section, we report the results of experiments where the pressure required to achieve the experimental mole fraction of dissolved gas is greater than P^{sat} . In this system, the fugacity of the dissolved gas is much greater than the equilibrium fugacity and the system is metastable with respect to hydrate formation. Thermodynamically, hydrates should obviously form from such metastable single-phase systems and they do form as the experiments demonstrate.

More interesting is the formation of hydrates from sub-saturated systems where X_i (the mole fraction of hydrate former in the water-rich liquid phase) is less than X_i at the three-phase equilibrium pressure $P_{\text{VLH}}^{\text{sat}}$. To form hydrates at equilibrium conditions from a single water-rich liquid phase (L₁H equilibria), P must be greater than $P_{\text{VLH}}^{\text{sat}}$ and the fugacity of the hydrate former must be greater than $f_{i,\text{VLH}}^{\text{sat}}$. Thermodynamically, pressure increases have a small effect on the fugacity of liquid phase species as illustrated in Fig. 1, which shows the fugacity of CO₂ as a function of pressure for a fixed temperature (275 K). For the purposes of this illustration only, an estimated value for \bar{V}_i for CO₂ of 40 cm³/mol is used (Teng, Yamasaki, Chun, & Lee, 1997). In this figure, X_i represents the overall mole fraction of CO₂ in the CO₂/water system. At pressures above P^{sat} there is only one phase present and X_i represents the mole fraction in the water-rich liquid. Note that the increase of fugacity with pressure is much greater when a gas phase exists ($P \leq P^{\text{sat}}$) and the

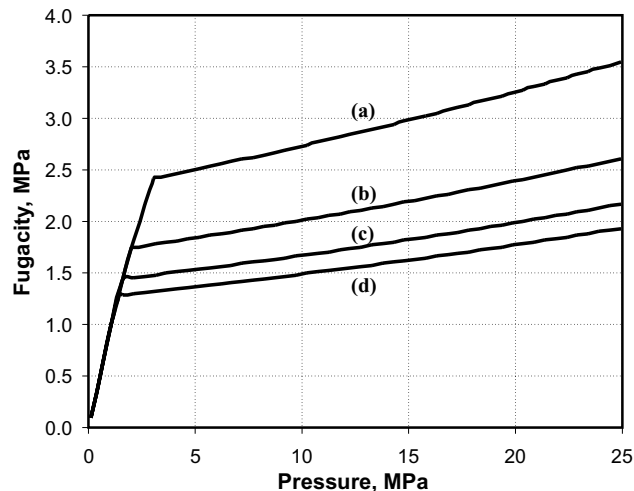


Fig. 2. The fugacity of CO₂ as a function of pressure for different compositions. Lines (a)–(d) represent calculations for water in the hydrate phase at a saturation pressure, P^{sat} , and mole fraction of dissolved CO₂, X_i , respectively, of: (a) 3.0 MPa, 0.026; (b) 2.0 MPa, 0.020; (c) 1.6 MPa, 0.019; (d) 1.4 MPa, 0.016. Above P^{sat} , only dissolved CO₂ is present. Below P^{sat} , CO₂ exists as a gas. $T = 275$ K. $\bar{V}_i = 40$ cm³/mol (estimated).

increase in fugacity with pressure is relatively modest when $P \geq P^{\text{sat}}$.

As shown in Fig. 2, the fugacity of CO₂ is the same regardless of ultimate liquid-phase composition until the CO₂ completely dissolves at P^{sat} , which is different for different levels of CO₂ saturation. This is because the gas phase contains pure CO₂ up to the corresponding $P_{x_i}^{\text{sat}}$. The compositions used to construct Fig. 2 were chosen to represent values of X_i that were greater and less than those at the VLH point ($X_i = 0.0188$). Using the fugacities from Fig. 2 as the basis we can calculate the chemical potentials from Eq. (7) as shown in Fig. 3.

If we then overlay Eq. (9) onto Fig. 3, Fig. 4 is obtained. In this figure, the mole fraction of water, X_w , used for Eq. (9) is held constant at 0.984 ($= 1 - 0.016$). Point A very closely approximates the pressure (1.59 MPa) at which hydrates would form if excess CO₂ were present. This represents VLH equilibria. Point B represents the pressure (21.8 MPa) at which hydrates would form from a water-rich liquid containing 0.016 mol fraction CO₂. At the VLH point, the water-rich liquid would contain slightly more CO₂ ($X_i \cong 0.0188$). At all compositions less than that at the VLH point ($X_i < 0.0188$), hydrates could form from a water-rich liquid if the pressure was sufficiently high. This is shown in Fig. 5, which gives the pressure required to form hydrates for various amounts of dissolved CO₂ at 275 K. As the mole fraction of CO₂ decreases, the pressure required to form hydrates will increase. For mole fractions greater than 0.0188, the amount of dissolved gas is greater than that which would exist at the VLH point and hydrates will form at all pressures

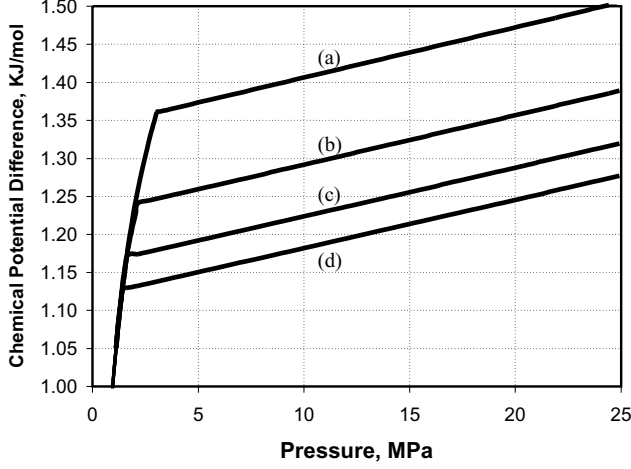


Fig. 3. Chemical potential difference of water in the hydrate phase from Eq. (7). Note that this chemical potential difference increases when the chemical potential of water decreases. The hydrate phase may be or may not be metastable. See Fig. 2 legend for definitions of lines (a)–(d). $T = 275 \text{ K}$, $\bar{V}_i = 40 \text{ cm}^3/\text{mol}$ (estimated).

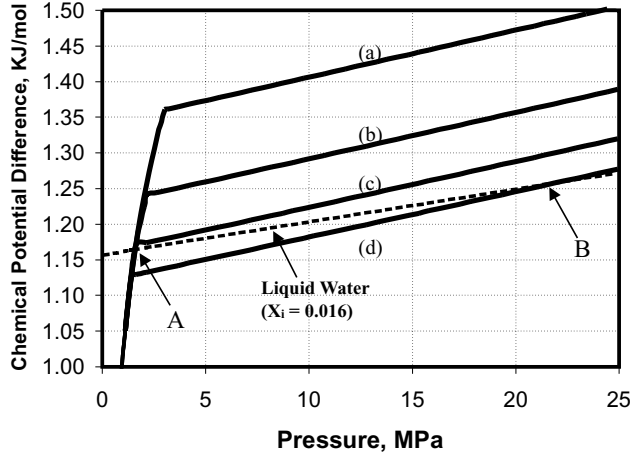


Fig. 4. Chemical potential difference of water in the hydrate and aqueous phases. The points of intersection A and B are equilibrium points for VLH equilibria and LH equilibria, respectively. See Fig. 2 legend for definitions of lines (a)–(d). $T = 275 \text{ K}$, $\bar{V}_i = 40 \text{ cm}^3/\text{mol}$ (estimated).

where this level of solubility can be obtained. However, this level of solubility cannot be obtained at pressures below the VLH pressure.

From Fig. 4, it is clear that the formation of hydrates from a subsaturated water-rich liquid requires the slope of the chemical potential of liquid water vs. pressure from Eq. (9) be less than the slope of the chemical potential of hydrate water vs. pressure from Eq. (7).

Mathematically, this requirement can be expressed as

$$\frac{\partial(\Delta\mu_H/RT)}{\partial P} > \frac{\partial(\Delta\mu_L/RT)}{\partial P}. \quad (10)$$

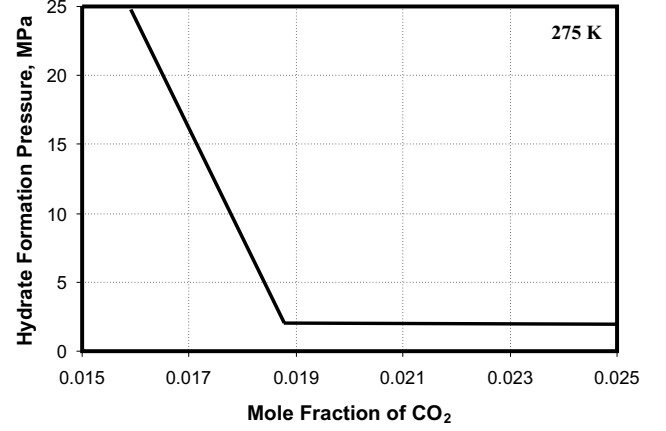


Fig. 5. Pressure required to form hydrates as a function of the overall mole fraction of CO_2 in a CO_2 water system at 275 K . Hydrates are predicted to form in the region of the line.

These derivatives can be calculated as follows:

$$\frac{\partial(\Delta\mu_H/RT)}{\partial P} = \sum_{j, \text{cavities}} \left[\frac{v_j \sum_i [C_{ji} f_i (V_i/RT)]}{1 + \sum_i C_{ji} f_i} \right]. \quad (11)$$

For a single hydrate forming gas:

$$\frac{\partial(\Delta\mu_H/RT)}{\partial P} = \frac{v_1 [C_{11} f_1 \bar{V}_1/RT]}{1 + C_{11} f_1} + \frac{v_2 [C_{21} f_1 \bar{V}_1/RT]}{1 + C_{21} f_1}. \quad (12)$$

For $C_{ji} \gg 1$ and with both cavities filled, the equation simplifies (in most instances $\theta_{ji} > 0.9$ and $C_{ji} > 9$)

$$\frac{\partial(\Delta\mu_H/RT)}{\partial P} = (v_1 + v_2) \frac{\bar{V}_i}{RT} \quad \text{if } C_{ji} \gg 1. \quad (13a)$$

If only the large cavity is occupied

$$\frac{\partial(\Delta\mu_H/RT)}{\partial P} = v_2 \frac{\bar{V}_i}{RT}. \quad (13b)$$

For structure I, $v_1 = 1/23$, $v_2 = 3/23$, for structure II, $v_1 = 2/17$, $v_2 = 1/17$ (Holder et al., 1988). The partial molar volumes of gases dissolved in water are $30\text{--}80 \text{ cm}^3/\text{mol}$ (Toplak, 1989). At 273 K the derivative's value will fall in a relatively narrow range:

$$\frac{\partial(\Delta\mu_H/RT)}{\partial P} \approx 0.001 - 0.005 \text{ 1/MPa}. \quad (14)$$

(Note: If only one cavity is filled, as for propane hydrate, the derivatives will be smaller, on the order of $0.001\text{--}0.002 \text{ 1/MPa}$).

For the liquid phase, estimates of the value of the derivatives can also be made:

$$\frac{\partial(\Delta\mu_L/RT)}{\partial P} = \frac{\Delta v}{RT} - \frac{1}{X_w} \frac{\partial X_w}{\partial P}. \quad (15a)$$

Table 1

Theoretical prediction of hydrate formation from single-phase aqueous systems containing various dissolved gases at 275 K^a

Gas	Hydrate Structure	\bar{V}_i (cm ³ /mol)	T_i (K) for \bar{V}_i	$\frac{\partial(\frac{\Delta\mu_L}{RT})}{\partial P}$ (1/MPa)	$\frac{\partial(\frac{\Delta\mu_L}{RT})}{\partial P}$ (1/MPa)	Hydrates form from liquid water
CH ₄	I	35	301	0.00266	0.00204	Yes
C ₂ H ₆	I	53	301	0.00302	0.00204	Yes
C ₃ H ₈	II	71	298	0.00183	0.00221	No
CO ₂	I	40	275	0.00304	0.00204	Yes
N ₂	II	36	291	0.00278	0.00221	Yes

^aPartial molar volumes and gas solubilities were obtained from the following literature sources: Wiebe and Gaddy (1940); Katz et al. (1959); Munjal and Stewart (1970); Prausnitz et al. (1986); Enick and Klara (1990).

But $X_i + X_w = 1$. Therefore,

$$\frac{\partial X_w}{\partial P} = - \frac{\partial X_i}{\partial P} \quad (15b)$$

since $X_w \approx 1.0$.

$$\frac{\partial(\Delta\mu_L/RT)}{\partial P} = \frac{\Delta v}{RT} + \frac{1}{X_w} \frac{\partial X_i}{\partial P} \approx \frac{\Delta v}{RT} + \frac{\partial(X_i)}{\partial P}, \quad (15c)$$

where (Holder et al., 1988)

$$\frac{\Delta v}{RT} \approx 0.002 \text{ 1/MPa}. \quad (16)$$

Since we are considering fixed composition liquid systems:

$$\frac{\partial X_i}{\partial P} \approx 0. \quad (17)$$

Thus,

$$\frac{\partial(\Delta\mu_H/RT)}{\partial P} > \frac{\partial(\Delta\mu_L/RT)}{\partial P} \quad (18)$$

will usually be true as required by Eq. (10) and hydrates can form from some sub-saturated aqueous systems. Table 1 gives examples based on the type of estimation described above for several hydrate-forming species. As can be seen, this simple method of estimation suggests that hydrates can often form from an aqueous liquid which has less dissolved gas than at the VLH point at the same temperature. However, absolute certainty requires a rigorous calculation as is illustrated in Fig. 4.

3. Experimental observations of hydrate formation from dissolved CO₂

Experimental observations of hydrate formation were made in a high-pressure, variable-volume viewcell (HVVC) that has been previously described (Warzinski, Lee, & Holder 1992; Warzinski et al., 1995). The HVVC is basically a small (40 cm³ maximum volume), windowed, high-pressure, cylindrical vessel that contains a movable piston that permits pressure control during an

experiment. A small, glass-encased magnetic stirring bar is used to promote mixing within the HVVC. The entire system is contained in a temperature-controlled air bath.

Various experiments have been made in the HVVC using both two-phase (water or seawater and gaseous or liquid CO₂) and single-phase (water or seawater containing dissolved CO₂) systems. While hydrate formation has been observed in various experiments using single-phase systems, two experiments will be described here that are pertinent to the subject of this paper. In these experiments, general purpose seawater (GPS) from Ocean Scientific International Ltd, Petersfield, Hampshire, UK, was used that had a salinity of 35. SFC-grade (99.99 + %) CO₂ was also used.

With the piston completely withdrawn, a vacuum was applied to the HVVC using a mechanical pump. Using a reservoir and balance, GPS was then added to fill the evacuated HVVC (about 46 g). The piston was then pushed in to expel water back to the reservoir until about 25 g remained in the HVVC. This evacuation and filling procedure ensured complete filling of the cell and connecting tubing. The piston was then pushed in to pressurize the cell and check for any leaks. The CO₂ was then added using an ISCO 260D syringe pump that was maintained at 10 MPa. The weight of CO₂ added was then determined using the density for CO₂ obtained from the IUPAC International Thermodynamic Tables of the fluid state for carbon dioxide at this pressure and the temperature of the laboratory (measured using a platinum resistance thermometer). The HVVC was then cooled to 285 K with stirring while the pressure was maintained near 20 MPa to facilitate the dissolution of the CO₂ into the seawater. After complete dissolution of the CO₂, the temperature and pressure were adjusted to the desired experimental conditions.

In one experiment, hydrate readily formed from a single-phase solution that initially contained 59 mg of CO₂ per gram GPS ($X_i = 0.024$) with agitation at 277 K and 15 MPa; conditions of temperature and pressure similar to those anticipated for deep ocean injection. The hydrate that formed was ice-like (transparent) in appearance and was more dense than the remaining aqueous phase. At this temperature and pressure, the predicted mole

fraction of CO₂ required for hydrate formation, X_i^{sat} , is 0.018. In another experiment in which the dissolved CO₂ concentration was near this level (44 mg CO₂ per gram GPS) hydrate did not form under similar conditions of temperature and pressure. However, hydrate did form in this solution at 275 K and pressures approaching 27 MPa. At this temperature and pressure, X_i^{sat} is estimated to be 0.016. The hydrate that formed was again more dense than the remaining seawater phase. Experiments are continuing at NETL to better define the phenomenon of hydrate formation from solutions subsaturated with CO₂ relative to that required for hydrate formation.

Experiments were recently reported by Buffett and Zatsepina (2000) in which hydrates were formed in porous media from dissolved CO₂ in contact with a non-equilibrium gas phase. The pressure of the gas phase adds some ambiguity to the experiment since the degree to which the gas concentration changed due to dissolution is unclear. The conditions of their experiment were such that the mole fraction of dissolved gas ($X_i = 0.013$, $T = 273.7$ K) was nearly identical to the saturated gas mole fraction ($X_i^{\text{sat}} = 0.015$, $T = 273.7$ K) at the three-phase VLH conditions although the pressure was much higher than the three-phase equilibrium pressure ($P = 2$ MPa, $P^{\text{sat}} = 1.2$ MPa). This experiment suggests that hydrates can form with less dissolved gas than would be present at three-phase saturation conditions. The current analysis verifies that this is indeed possible.

4. Conclusions

It is clear from both theoretical and experimental evidence that hydrates can form from dissolved gas in the absence of a free-gas phase. Experiments show that CO₂ hydrate will form when no gas phase is present when the solution contains excess dissolved CO₂. The mathematical analysis presented in this paper can also be verified using liquid water-hydrate flash calculations from Gibbs free energy minimization hydrate prediction models. Conventional models can be modified to predict the hydrate formation pressure as a function of the amount of dissolved CO₂ allowing for the design of experiments or processes utilizing this phenomenon.

Notation

C_{ji}	Langmuir constant for species i in cavity j
f_i	fugacity of hydrate-forming species i , MPa
$f_{i,L}$	fugacity of hydrate-forming species i in liquid phase, MPa
$f_{i,H}$	fugacity of hydrate-forming species i in hydrate phase, MPa
f_i^{sat}	fugacity of hydrate-forming species i at P^{sat} , MPa

P	pressure, MPa
P^{sat}	bubble-point pressure, MPa
R	gas constant
T	temperature, K
T_0	reference temperature, K
\bar{V}_i	partial molar volume of species i in water phase, cm ³ /mol
X_i	mole fraction of gas species in liquid phase
X_w	mole fraction of water in the water-rich liquid phase
Δh	enthalpy difference between empty hydrate and pure liquid water
Δv	volumetric difference between empty hydrate and pure liquid water

Greek letters

$\Delta\mu^0$	reference chemical potential of hydrate former, kJ/mol
$\Delta\mu_H$	chemical potential difference of water in hydrate phase, kJ/mol
$\Delta\mu_L$	chemical potential difference of water in liquid phase, kJ/mol
θ_{ji}	fraction of j -type cavities occupied by i -type gas molecules
μ_H	chemical potential of water in hydrate phase, kJ/mol
μ_L	chemical potential of water in liquid phase, kJ/mol
μ^β	chemical potential of hypothetical empty hydrate lattice, kJ/mol
v_j	ratio of j -type cavities present to number of water molecules present in the hydrate phase

References

- Buffett, B. A., & Zatsepina, O. Y. (2000). Formation of gas hydrate from dissolved gas in natural porous media. *Marine Geology*, 164, 69–77.
- Enick, R. M., & Klara, S. M. (1990). CO₂ solubility in water and brine under reservoir conditions. *Chemical Engineering Communications*, 90, 23–33.
- Holder, G. D., Corbin, G., & Papadopoulos, K. D. (1980). Thermodynamic and molecular properties of gas hydrates from mixtures containing methane, argon and krypton. *Industrial and Engineering Chemistry Fundamentals*, 19, 282–286.
- Holder, G. D., Zetts, S. P., & Pradhan, N. (1988). Phase behavior in systems containing clathrate hydrates, a review. *Reviews in Chemical Engineering*, 5(1–4), 1–70.
- Katz, D. L., Cornell, D., Kobayashi, R., Poettmann, F. H., Vary, J. A., Elenbaas, J. R., & Weinaug, C. L. (1959). *Handbook of natural gas engineering*. New York: McGraw-Hill.
- Munjial, P., & Stewart, P. B. (1970). Solubility of carbon dioxide in pure water, synthetic sea water and synthetic sea water concentrates at -5°C to 25°C and 10 to 45 atm pressure. *Journal of Chemical and Engineering Data*, 15(1), 67–71.
- Peng, D. Y., & Robinson, D. B. (1976). A new two-constant equation of state. *Industrial and Engineering Chemistry Fundamentals*, 15(1), 59–64.

- Prausnitz, J., Lichtenthaler, R. N., & Gomes de Azevedo, E. (1986). *Molecular thermodynamics of fluid-phase equilibria* (2nd ed.). Englewood Cliffs, NJ: Prentice-Hall, Inc.
- Sloan Jr., E. D. (1998). *Clathrate hydrates of natural gas* (2nd ed.). New York: Marcel Dekker.
- Sloan Jr., E. D., Khoury, F. M., & Kobayashi, R. (1976). Water content of methane gas in equilibrium with hydrates. *Industrial and Engineering Chemistry Fundamentals*, 15(4), 318–323.
- Song, K. Y., & Kobayashi, R. (1982). Measurement and interpretation of the water content of a methane–propane mixture in the gaseous state in equilibrium with hydrate. *Industrial and Engineering Chemistry Fundamentals*, 21, 391–395.
- Toplak, G. J. (1989). *Solubilities of hydrocarbon gas mixtures in distilled water near hydrate forming conditions*. M.S. thesis, Department of Chemical and Petroleum Engineering, University of Pittsburgh.
- Teng, H., Yamasaki, A., Chun, M. K., & Lee, H. (1997). Solubility of liquid CO₂ in water at temperatures from 278 K to 293 K and pressures from 6.44 MPa to 29.49 MPa and densities of the corresponding aqueous solutions. *Journal of Chemical Thermodynamics*, 29, 1301–1310.
- Warzinski, R. P., Lee, C.-H., & Holder, G. D. (1992). Supercritical-fluid solubilization of catalyst precursors: The solubility and phase behavior of molybdenum hexacarbonyl in supercritical carbon dioxide and application to the direct liquefaction of coal. *Journal of Supercritical Fluids*, 5, 60–71.
- Warzinski, R. P., Cugini, A. C., & Holder, G. D. (1995). Observations of CO₂ clathrate hydrate formation and dissolution under deep-ocean disposal conditions. In J.A. Pajaras, & J.M.D. Tascón (Eds.), *Coal science* (pp. 1931–1934). Amsterdam: Elsevier.
- Wiebe, R., & Gaddy, V. L. (1940). The solubility of carbon dioxide in water at various temperatures from 12°C to 40°C and at pressures to 500 atmospheres. Critical phenomena. *Journal of the American Chemical Society*, 60, 815–817.